Cleantan – Chromium Tanning Without Chromium and Water Residues*

by

Manfred Renner,** E. Weidner and H. Geihsler

Fraunhofer Institute UMSICHT,

Oberhausen, Germany

Abstract

Fraunhofer UMSICHT has developed a new chromium tanning process principle to reduce the chromium contaminated sewage water, to save tanning agents and to reduce the process time. The first part of the lecture, given by Manfred Renner, head of business unit, will give a survey of the new tanning principle. The compressed natural gas carbon dioxide is used instead of water for the pickling and the tanning process. The use of different pressure ranges gives the possibility to control the pH value without using chemicals. A free from water and free from salt pickle is possible. The use of chromium can be controlled precisely and it is possible to use only as much chromium as can be fixed in the collagenic matrix. The lecture will show results achieved with technical- and preindustrial scale (650 kg split weight per batch) high-pressure equipment.

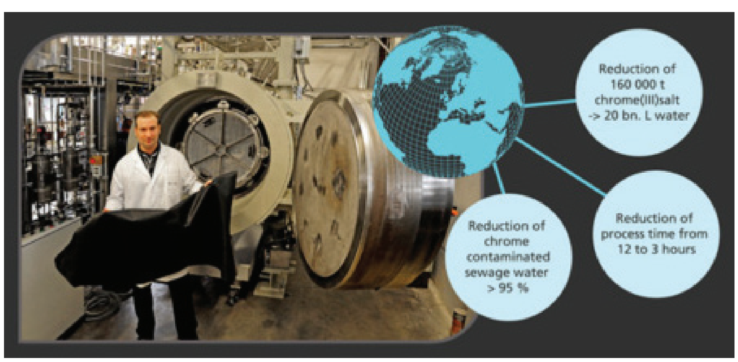
Using carbon dioxide 14 million liters of chromium contaminated sewage water in the tanning process, 20 billion liters of sewage water to produce the tanning agents, 160 000 tons of chromium and 500 000 tons of salt could be saved regarding the worldwide market.

The second part of the lecture, given by Prof. Dr. Weidner, head of the Fraunhofer Institute UMSICHT, will focus on the strategy of how to enter the market. For the prospective customers it will give the opportunity to see if the technology fits their companies and their main OEM customers. It will also be shown how easy the new equipment can be implemented in a running tannery.

Resumen

Fraunhofer UMSICHT ha desarrollado un nuevo principio del proceso de curtido al cromo para reducir el cromo en aguas residuales contaminadas, para ahorrar curtientes y reducir el tiempo de proceso. La primera parte de la conferencia, a cargo de Manfred Renner, director de la unidad de negocio, le dará una visión del nuevo principio de curtido. El dióxido de carbono del gas natural comprimido se utiliza en lugar del agua de pickelado y del proceso de curtido. El uso de diferentes rangos de presión da la posibilidad de controlar el valor del pH sin necesidad de utilizar productos químicos. Un pickelado libre de agua y de sal es posible. El uso de cromo puede ser controlado con precisión y es posible utilizar sólo la cantidad de cromo que puede ser fijado en la matriz de colágeno. La conferencia mostrará los resultados obtenidos a escala técnica y preindustrial (650 kg de peso dividido por lote) en equipos de alta presión. Mediante el empleo de dióxido de carbono, 14 millones de litros de agua contaminada con aguas residuales de cromo del proceso de curtido, 20 mil millones de litros de aguas residuales para producir los agentes de curtido, 160.000 toneladas de cromo y 500.000 toneladas de sal pueden ahorrarse en relación al mercado mundial.

La segunda parte de la conferencia, a cargo de Prof. Dr. Weidner, director del Instituto Fraunhofer UMSICHT, se centrará en la estrategia de cómo entrar en el mercado. Para los clientes potenciales se le dará la oportunidad de ver si la tecnología se adapta a sus empresas y sus principales clientes OEM. También se muestra lo fácil que el nuevo equipo puede implementarse en una curtiduría en funcionamiento.



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**Corresponding author e-mail: manfred.renner@umsicht.fraunhofer.de

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INTRODUCTION

Over 2000 km^2 of leather are produced every year. To produce this amount, about 7 million tons of skin, 500,000 tons of salt, 500 000 tons of chromium-III-salt are needed. Approximately 90% of all leather is tanned by using chromium-III-salts. After China the EU is the second largest producer in the world. In 2007 the European tanneries produced approx. 325 million square meters in 1650 tanneries with 26 000 employees.[1-3] Leather manufacturing is extremely intensive with respect to raw materials and work. According to estimations the costs of environmental protection measures in European tanneries account for approx. 5% of their turnover.[4] The high amount of consumables and chemicals used illustrates the enormous demand for an intensified and environmentally friendly process. The high consumption of fresh water, mostly drinking water, and the strong contamination of water strongly influence on the perception of leather as a "natural product." The new process principle described in the following combines advantages of the conventional method, mainly high quality, with the possibility of considerable savings in process time, chemicals and water.

The following section provides a brief overview on the most relevant process steps of the conventional tanning process. Tanning methods can be categorized into three groups regarding the tanning agents. It is possible to tan with metal salts like chromium and aluminum, vegetable tanning agents like quebracho and tara and synthetic tanning agents like syntane. During the process the skin has to be prepared for an optimal absorption of the tanning agent into the skin prior to cross-bonding between skin collagen and tanning agent.[5-8]

CO_2-intensified tanning process

The basic idea of the new process is to carry out the tanning step under the pressure of CO_2. Limed and pickled skins were provided by a tannery as whole or in parts as described below. The skins were put into contact with tanning solutions. In initial experiments, a surplus of tanning solution was applied. The dependency of chromium content and shrinkage temperature from the time of tanning and pressure was investigated. In the course of the development an optimized method was found, where the amount of water was minimized, resulting in a process practically free of wastewater. For that purpose a part of the water present in the skin after the pickling step was removed. This water was replaced by tanning solution 2. The skin thus pretreated was introduced into high pressure equipment and treated under different pressures at varying contact times. The quality was assessed either by measuring the chromium content and/or shrinkage temperature. For both procedures it was found that leather of very high quality could be obtained at a drastically reduced time of contact by carrying out the tanning step above a certain pressure of CO_2. Additionally, wastewater, containing chromium can be reduced to almost zero.

MATERIAL AND METHODS

Tanning solutions

Similar to conventional tanning, chromium-III-salt was used as tanning agent for all experiments. The tanning solution consisted of water, chromium-III-salt, salt, formic and sulphuric acid. In the tanning industry all weights are related to the weight of the wet skin before the tanning step (example: 150 g water on 100 g wet skin means 1:1.5). Tanning solution 1 consisted of 1:10 water, 1:0.09 chromium-III-salt, 1:0.005 formic acid, 1:0.008 sulfuric acid and 1:0.12 sodium chloride. That means that a mass of wet skin of 1 kg is contacted with 10 kg of water, 0.09 kg tanning agent, 0.005 kg of formic acid, 0.008 kg of sulfuric acid and 0.12 kg of salt. Tanning solution 2 consisted of 1:0.3 water (previously removed from the wet skin), 1:0.05 chromium-III-salt, 1:0.0003 formic acid and 1:0.0003 sulfuric acid. That means that from 1 kg mass of wet skin a mass of 0.3 kg of water is removed and replaced by 0.3 kg of water, 0.09 kg of tanning agent, 0.0003 kg of formic acid and 0.0003 kg of sulfuric acid.

Skin

An average cattle skin has a surface area of 7 to 9 m^2. It is divided into several parts. The part with the highest quality and the most regular structure is the so-called "croupon." The neck and the croupon were taken for this work. The neck had a thickness of 2 to 2.4 mm and the croupon one of 2.6 to 3 mm. Both were obtained by splitting the whole skin with a band knife. The neck was taken as one part per trial (area of about 0.25 m^2). The croupon was divided into 5 parts (with an area of about 0.2 m^2 per part).

Quality assessment

Chromium tanned leather has to be resistant against boiling water without degeneration of the collagenous structure. As cooking stability is most commonly used in industry, the quality assessment of wet-blue in this work was carried out by measuring the shrinkage temperature. After the tanning process a defined part of the leather was punched out. This sample was placed firmly with an interlock on one side of the apparatus. The other side was connected by a yarn using a hook. A weight tightened the system. The sample was subsequently submerged into water. The water was heated up until it boiled. When the leather sample shrunk at a temperature below 100°C the quality was not sufficient. The samples were also tested on their chromium content by using emission spectrometry. 4 weight percent should be reached.

20 L high pressure tanning bin

The PLC-controlled "pilot-scale plant" shown in figure 1 was especially build for high pressure tanning. Inside the horizontal autoclave a rotatable cage can be used for tanning comparable to industrial procedures. In order to ensure that the skin moves around continuously inside the cage some metal pins were screwed in vertically. The motion is relevant for mass transport and regularity of the chromium distribution. The maximum working parameters were 320 bar, 80°C and 20 rpm.

1,700 L high pressure tanning bin

To carry out test series in preindustrial scale a "demonstration plant" with a volume of 1,700 L was build. The autoclave is also positioned horizontally. A mass of up to 700 kg (> 100 m^2 leather) can be tanned per batch in a rotating drum. The design of the drum is comparable to conventional pressure-less tanning bins. The use of pins, mounted to the inner side of the rotating drum, intensifies the motion of the skins and thus a good contact of gas and tanning agent. The equipment allows the feeding of tanning liquids against pressures of up to 260 bar.

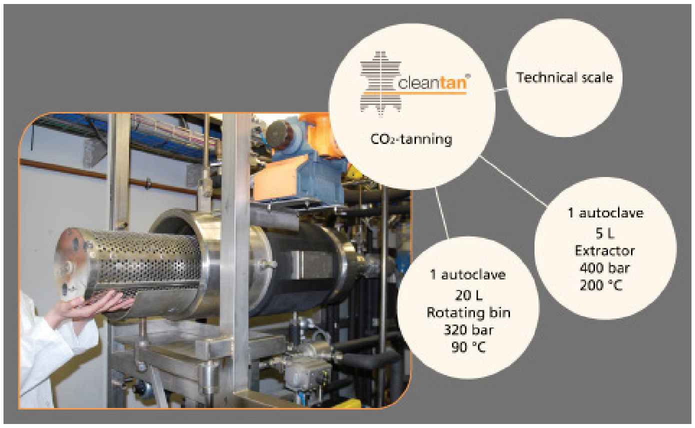

Figure 1: Technical scale equipment

RESULTS

Chromium tanning under CO_2-pressure as function of pressure and contact time

A shortening of process time from 30 to 5 hours using carbon dioxide at 100 bar could be proved in lab-scale. Chromium content and maximum uptake of 3.6 wt.-% chromium are comparable to industrial values.[9] Similar observations in lab-scale have been published by other work groups.[10-12] The results were transferred into pilot-scale. The skin samples weighted about 700 to 900 g. The tanning sessions were carried out with the same tanning solution to hide mass ratios as in laboratory scale. The basket rotation was set to 10 rpm and the hide was pulled continuously through the tanning solution as is done in the conventional process. Tanning sessions that produced high leather quality are shown in the form of plus signs, and those that produced lower quality in the form of minus signs. Figure 2 shows that tanning time can be shortened to 2.5 h using 200 and 300 bar and to 3 h using 100 bar. The main focus of the investigation was on whether the shrinkage criterion of cooking stability was reached or not. It became apparent that at 300 bar, no significant reduction of the tanning time versus 100 bar could be achieved.

Tanning free of chromium contaminated wastewater

One of the most important problems of the tanning industry is the wastewater after the tanning step, which is highly charged with chromium and salt. The objective of the investigation presented in this chapter was the reduction of chemicals and chromium contaminated wastewater. The results shown in

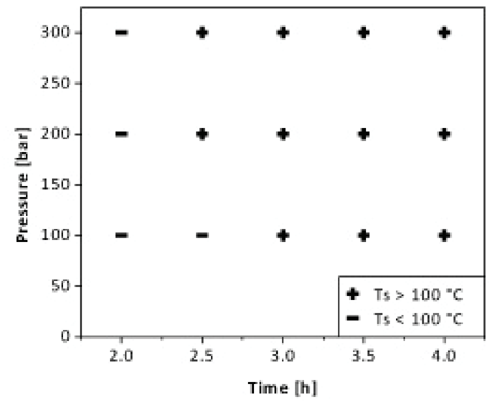

Figure 2: Process time using CO_2 as process intensifier

figure 3 were obtained in a modified process. The skins were partly de-wetted mechanically before tanning. This removed mass was substituted by tanning solution 2, which was soaked up into the skin in 30 min. Tanning those skins in our equipment without applying gas pressure, results in bad quality.

For carrying out experiments under pressure, the soaked skin was introduced into the pressure vessel and CO_2-pressure was built up in some minutes. During the high-pressure process the chromium ions diffuse to the reactive sites of the skin collagen. Figure 3 shows the influence of pressure and time. The values for 100 bar were taken from figure 2 and are used to compare the results obtained with solution 1 and solution 2. It can be seen that the tanning time can be further reduced, even at lower pressures. The trials carried out at 20 bar of carbon dioxide pressure failed to produce high leather quality. A threshold pressure could be identified at 30 bar. At a time of 2 h at 30 bar and at 50 bar positive and negative results were achieved, indicated by overlapping of plus and minus in figure 3. As mentioned in chapter 2 different parts of the skin have been tanned. Some parts were of high quality even after 2 h, while others did not reach sufficient cooking stability. At such low times, variations in skin properties (pore distribution, fiber compactness) are of relevance for the tanning results. At contact times of 2.5 h and beyond, all parts (either from croupon or neck) were of high quality.

A wastewater reduction of more than 95% was achieved with this approach. With a conventional tanning process, approx. 1 to 2 tons of chromium loaded water is generated during the production of one ton of leather. The new method produces less than 10 kg of wastewater per ton of leather. The amount of chromium-III-salt used can be reduced by about 45%, the amount of sulfuric and formic acid by about 95%. The further reduced process time can be attributed to the greater surface area available for the diffusion of carbon dioxide. In the approach applied in lab-scale experiments, lower parts of the hide were immersed in the tanning solution, while the upper side was in direct contact with CO_2. The gas could predominantly diffuse into the skin via the upper side. In pilot-scale, experiments (figure 2) with "free-flowing tanning"

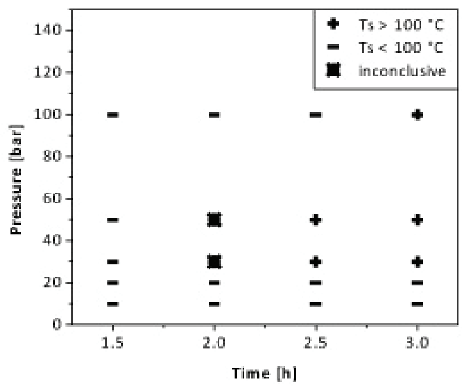

Figure 3: Process time at different pressures

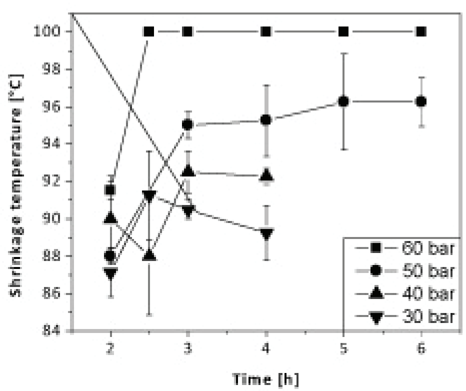

Figure 4: Ts by variation of pressure and time

solution 1 were performed. In difference to lab-scale, the skins were moved by means of the rotating drum, thus repeatedly exposing both upper and lower side of the skin surface to CO_2. By this effect, the required contact time for a good quality was reduced from 5 h in lab-scale to 3 h in pilot scale. In a second approach, no free flowing liquid (tanning solution 2) was present in the autoclave. The samples were moved mechanically. Due to the lack of free liquid, they have been in continuous contact with the gas phase. This method resulted in a further (slight) reduction of tanning time (3 h to 2.5 h). Even more important than time saving is the avoidance of waste water and the reduction of the required amount of chromium and salt by applying this modified tanning process.

Influence of pressure using a minimum of chemicals for different parts of skin

The aim of this investigation was to identify conditions for the tanning of all parts of skin with varying cross sections and fiber compactness. The ratio of masses was calculated as shown in chapter 2. For each point in figure 4 four samples were produced and assessed. The average weight of the samples was around 600 g. A process time of 2 h results in leathers with a shrinkage temperature (T_S) between 86 and 92°C. For 30 and 40 bar T_S does not increase above 93°C at a tanning of 4 h. Using 50 bar T_S can be increased to 95 to 97°C at a tanning time between 3 and 6 h. A shrinkage temperature of 100°C can be obtained after 2.5 h and 60 bar for all investigated parts of the skin. All 20 samples showed cooking stability.

Discussion and Conclusions

In lab-scale and pilot-scale tanning time could be shortened by factors of 3 to 6 using CO_2 as process intensifier at 100 bar. Further trials in pilot-scale show that increasing pressure from 100 to 300 bar has no significant influence. Regarding the tanning time the mass of the liquid phase in the autoclave looms large. The larger the area for the diffusion of compressed carbon dioxide into the skin the shorter the time needed for tanning is. In a new approach it was found that a surplus of liquid in the autoclave could be avoided if tanning is carried out under CO_2-pressure. In that case the tanning time could be shortened to 2.5 to 3 h. On the one hand reducing the water content requires an adaptation of the concentration of chromium salts in the tanning solution, to achieve a sufficient quality of the leather. Absorbing water with a high chromium content into partly de-wetted skins results in a higher concentration gradient of chromium. Thus diffusion is accelerated. On the other hand the skin matrix is most likely widened by CO_2. This behavior was investigated for several complex solids, including certain biopolymers.[13-18] Regarding the sizes of chromium polynucleate complexes diffusing into the skin; a slight widening has a great influence on penetration. The chromium complexes have a size of about 0.75 nm and 1.29 nm.[19] According to Nishad,[20] Covington[21] and Braeumer,[22] penetration is not the time limiting step, but most of the process time is taken by the diffusion inside the collagen microfibrils.[23] The polynucleate complexes have to diffuse between the fibrils for reaching reactive binding sites.[24] The gap between the microfibrils is estimated to be 1.4 nm.[25] The "diffusion tunnels" in the fibrils can take up a length of several centimeters.[26-28] Having no liquid phase inside the autoclave the CO_2 can penetrate directly over the surface into the skin. This way the mass transport is influenced positively.

New trials carried out at Fraunhofer UMSICHT using a demonstration plant (1 750 L autoclave volume, Fig. 5) with a rotating drum showed very promising results. A mass of over 500 kg per batch can be treated now. It was found that lower

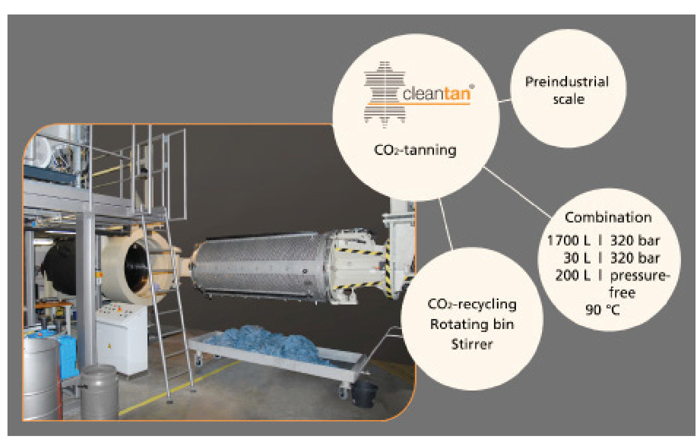

Figure 5: Preindustrial scale equipment

pressure than in pilot scale resulted in very high leather quality, probably because of an intensified flexing of the material. Flexing is improved from smaller to bigger skins, which are able to twist. The torsion seems to improve the mass transport of tanning solution and CO_2 additionally. This assumption is confirmed by know-how from conventional tanning.[29]

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